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UO_2 sintering in controlled oxygen atmospheres of three-stage process

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Abstract

The sintering of UO_{2+x} in oxidizing atmospheres was studied using a three-stage sintering process in order to obtain a large grain pellet from UO_2 powder converted by conventional ADU. The three-stage process consists of sintering in reducing–oxidizing–reducing atmospheres at low temperatures between 1200 and 1500°C. After the sintering temperature was reached, the atmosphere was changed from a reducing to an oxidizing one in which the oxygen partial pressure was controlled to the maximum value corresponding to the boundary between the single-phase region UO_{2+x} and the two-phase region UO_{2+x}–U_3O_{8-z}. The densification and grain growth of UO_{2+x} are enhanced by increasing the oxygen partial pressure. Air could be used above 1500°C. The O/U ratio of the sintered pellets was 2.000 ± 0.005 after reducing in the subsequent reducing atmosphere of H_2/N_2 (= 1/2) mixture for 1 h followed by cooling-down. The thermal dimensional changes during resintering at 1700°C of a UO_2 pellet sintered in the three successive atmospheres of H_2–CO_2–H_2 at 1400°C resulted in a moderate densification, whereas a large degree of swelling occurred in a pellet sintered in CO_2–H_2.

1. Introduction

UO_2 pellets are generally manufactured by cold-pressing and sintering methods. One way of improving the performance of high burnup fuel for light water reactors, is to use a large grain UO_2 pellet which is expected to give a smaller fission gas release [1]. On the other hand, many studies have been performed with the purpose of reducing the sintering temperature and so reducing manufacturing costs. Generally, the sintering of UO_2 pellets is carried out in H_2 atmosphere at high temperatures above 1700°C using a single-stage sintering process as shown in Fig. 1. Langrod [2] and Fuhrman et al. [3] showed that UO_2 pellets, produced by a two-stage low-temperature pellet-fabrication process, could be sintered to at least 95% TD (theoretical density) at 1200°C in an inert (N_2) atmosphere and the minimum initial O/U ratio required to achieve such a density was 2.25 which was obtained by the oxidation of UO_{2+x} powder. In order to assure complete removal of the excess oxygen, a hydrogen soaking period of 1 h was required at 1200°C. German researchers [4–6] and Chevrel et al. [7] indicated that the oxidizing sintering in a two-stage process could be carried out in CO_2 atmosphere at low temperatures in a short period of time. They showed that the composition of $UO_{2.25}$ appeared to be the most appropriate for the low-temperature sintering. This $UO_{2.25}$ oxide was obtained by addition of U_3O_8. Reduction of the as-sintered uranium oxide pellet was done by changing the atmosphere to H_2 for a short period. Korean researchers indicated that UO_2 pellets, produced by single-stage [8] and two-stage processes [9,10], could be sintered easily by heating in an atmosphere of CO_2/CO mixture gas and in the flowing gas which was changed from CO_2 to H_2 at low temperatures, respectively. The gases which had oxygen partial pressures higher than that of conventional CO_2 gas were not used for the reaction in the oxidizing atmosphere of the above two-stage process.

This paper describes the sintering behaviour of hyper-

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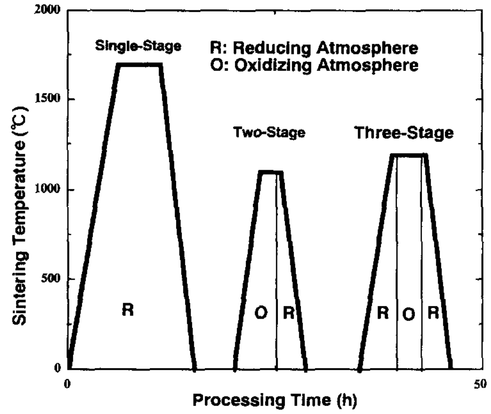

Fig. 1. Comparison of reducing and oxidizing sintering processes for UO_2 pellets.

stoichiometric uranium oxide in oxidizing atmospheres of which the oxygen partial pressures are higher than that of CO_2 gas using a three-stage sintering process [11,12] at low temperatures.

2. Experimental procedures

In this study, UO_2 powders produced by the conventional ADU (ammonium diuranate) conversion process were used. The O/U ratios were from 2.08 to 2.12 and the specific surface areas, measured by the BET method, were from 2.27 to 2.40 m^2/g. The powders were 99.9% pure, with the major impurities being carbon and fluorine. Green pellets were prepared by conventional techniques which involved prepressing the powder to 5.0 g/cm^3 at 1 ton/cm^2, granulating to produce a flowable feed powder (slugging), blending with die lubricant (0.2 wt% zinc stearate) and pressing cylindrical pellets to 6.0 g/cm^3 at 4 ton/cm^2. The sintering processes are shown schematically in Fig. 1. In the conventional single-stage process, these green pellets were heated at a rate of 300°C/h and then held at a high temperature (1750°C) for 5 h and finally cooled down to room temperature at a rate of 400°C/h in a wet H_2 atmosphere with dew points between 5 and 10°C ($P_{H_2O}/P_{H_2} \fallingdotseq 10^{-2}$) without changing the atmosphere. The two-stage process consisted of heating-up and heating for 2 h first in CO_2 atmosphere and second in a subsequent reducing atmosphere of H_2 at 1400°C for 1 h followed by cooling-down in H_2. The three-stage sintering process [11,12] was performed in a reducing atmosphere of H_2/N_2 ($= 1/2$) mixture during the heating-up and heating for 1 h and then in a subsequent oxidizing atmosphere of controlled oxygen partial pressures for 2 to 6 h. Lastly, the pellets were again treated in the same reducing atmosphere for 1 h at temperatures between 1100 and 1600°C followed by cooling-down. The used CO_2 gas was 99.7% pure, the impurities being about 0.05% O_2 and 0.2% N_2. To obtain the oxygen partial pressures lower than that of CO_2 gas, mixtures of CO_2/CO were used. The oxygen partial pressure was calculated from data published by Coughlin [13]. For the oxygen partial pressures higher than about 10^{-3} atm, mixtures of air/CO_2 or air/N_2 or air were used. The oxygen potential was maintained constant by flowing a gas of fixed air/CO_2 or air/N_2 ratios between 0.01 and 1. The mixed gases were introduced to the furnace through a static mixer. Before and after air was supplied, N_2 purge was carried out for 0.1 h. The pellets were sintered on a molybdenum tray for the conventional single-stage sintering and on an alumina tray for the two and three-stage sinterings. Also, the thermal resintering tests were carried out at 1700°C in a wet H_2 atmosphere ($P_{O_2} \fallingdotseq 5 \times 10^{-12}$ atm).

The densities of the sintered pellets were measured geometrically and reported as a percentage of the theoretical density of UO_2 (10.96 g/cm^3). The error in the measurements was estimated to be ±0.2% TD. The open porosities were measured by the water immersion method [14]. Its reproducibility was ±0.5 vol%. The O/U ratio was measured by oxidation to U_3O_8 with tolerances of ±0.005. The pore and grain structures were examined by ceramography and the average grain size was measured using the direct intercept method.

3. Results and discussion

3.1. Limit of oxygen partial pressure in the sintering atmosphere

Fig. 2 shows the appearance (i.e., the presence or absence of cracks) of UO_2 pellets heated at various temperatures and oxygen partial pressures in the second stage of the three-stage sintering for 1–6–1 h in reducing–

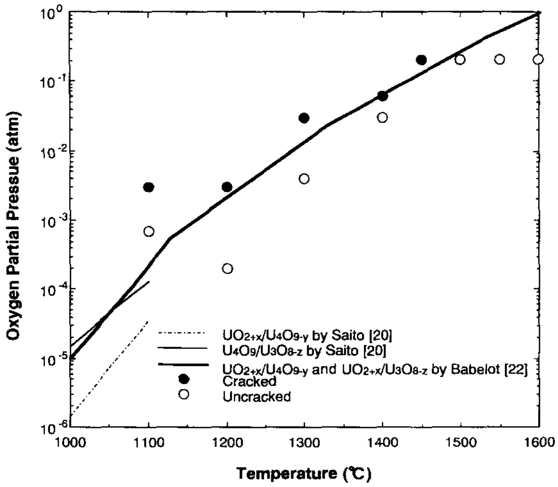

Fig. 2. Appearance of UO_2 pellets sintered for 6 h with different oxygen partial pressures and temperatures during the second stage.

oxidizing–reducing atmospheres. A range of sintering temperatures between 1100 and 1600°C was used during this second stage.

Many thermodynamic measurements and phase diagram determinations have been carried out on the U–O system [15–22]. The O/U limits of the UO_{2+x} (cubic) and U_3O_{8-z} (orthorhombic) phases were estimated to be 2.23 and 2.58, respectively, between 1000 and 1600°C by Chapman and Meadows [15]. The equilibrium oxygen partial pressure at which the UO_{2+x} and U_3O_{8-z} phases coexist, was found to depend on temperature in this temperature range. However, their experiments were incapable of detecting small compositional changes. No effort was made to distinguish U_4O_{9-y} from UO_{2+x} in their study. The boundary between a single phase region of UO_{2+x} and a two-phase region in the range of UO_{2+x}–$UO_{2.61}$, was found above 1200°C by Anthony et al. [16]. However, they did not check the U_4O_{9-y} to UO_{2+x} transition at 1125°C. Lierde et al. [17] proposed the homogeneity range of the U_4O_{9-y} phase from 2.235 to 2.240 at 1100°C, excluding the stoichiometric composition O/U = 2.250. Also, the U_4O_{9-y} to UO_{2+x} transition at 1125°C was interpreted as an order–disorder transformation. On the other hand, Matsui and Naito [18] suggested the existence of U_4O_{9+y} in the temperature range from 1025 and 1126°C and the peritectoid temperature ($U_4O_{9\pm y} = UO_{2+x} + U_3O_{8-z}$) between 1126 and 1131°C. The oxygen partial pressure at the phase boundary between U_4O_{9+y} and U_3O_{8-z} was obtained as 1.6×10^{-4} atm at 1100°C. The oxygen partial pressure on the UO_{2+x}–U_4O_9–U_3O_8 three phase equilibria, was obtained as 1.8×10^{-3} atm at 1127°C and then O/U = 2.240 by Nakamura and Fujino [19]. The equilibrium oxygen partial pressures for the single-phase region UO_{2+x} and the two-phase coexisting regions, UO_{2+x}–U_4O_{9-y} and U_4O_9–U_3O_{8-z}, were calculated from the empirical equation obtained by Saito [20] below 1100°C (Fig. 2). On the other hand, the O/U at the phase boundary of UO_{2+x} with the two-phase region UO_{2+x}–U_4O_{9-y}, was given by Rand et al. [21] as the interpolation between 2.22 and 2.24 at 1077 and 1127°C, respectively. Also, the O/U at the phase boundary of UO_{2+x} with UO_{2+x}–U_3O_{8-z} was given as the interpolation between 2.24 and 2.27 at 1127 and 1727°C, respectively. The equilibrium oxygen partial pressures for these upper phase boundaries of UO_{2+x} were calculated from the formula given by Babelot et al. [22] (Fig. 2). Cracks were found in UO_2 pellets sintered in oxygen partial pressures higher than the equilibrium values at the phase boundary, but not found in UO_2 pellets sintered in the pressures lower than the equilibrium values except 1100°C. The pellets sintered at 1100°C for 6 h, was not possible to reach equilibrium because a time longer than 12 to 24 h was necessary to reach equilibrium at about 1100°C [18]. The cause of this cracking can be attributed to a change in volume due to a fluorite–orthorhombic structure transition from UO_{2+x} to U_3O_{8-z} [23] above 1200°C.

The O/U ratios of these sintered pellets were 2.000 ± 0.005 after the following reduction at temperatures between 1100 and 1600°C for 1 h and in the process of the cooling-down. The integrity of the UO_2 pellets was not affected by this reduction. It is confirmed that air can be used in the second stage of the three stage sintering above 1500°C because the oxygen partial pressure of air is below the equilibrium value at the phase boundary of UO_{2+x} with the two-phase regions UO_{2+x}–U_3O_{8-z} at 1500°C. The limit of the oxygen partial pressure in the sintering atmosphere is the equilibrium value at the upper single phase boundary of UO_{2+x} at temperatures between 1200 and 1500°C. The effect of the oxygen partial pressure below the limit value on densification and grain growth will be discussed later.

3.2. Densification and grain growth

In the case of the UO_2 powders made by the conventional ADU process, the density and grain size of the UO_2 pellets sintered in wet H_2 atmosphere at 1750°C for 5 h using the conventional single-stage process, were above 95% TD and 7 to 9 μm, respectively. Fig. 3 shows the variation of the density of UO_2 pellets with the oxygen partial pressure in the sintering atmosphere during the second stage of sintering at 1400°C in the three-stage process. The data are plotted for two cases of 6 and 2 h (i.e., 1–6–1 h and 1–2–1 h processes). The density increases as the oxygen partial pressure is increased. The oxygen partial pressure needed to densify up to 95% TD when sintered at 1400°C for 1–2–1 h, was about 10^{-3} atm. The density, in the case of sintering for 1–6–1 h, levelled off at about 97% TD when the oxygen partial pressure increased above 10^{-3} atm. Fig. 4(a) shows the variation of grain size with the oxygen partial pressure for the UO_2 pellets sintered at temperatures between 1200 and

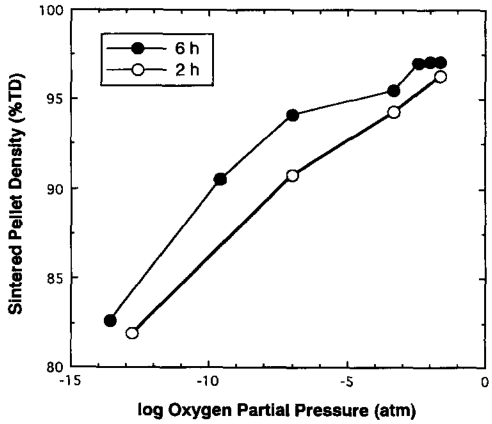

Fig. 3. Variation of density of UO_2 pellets with oxygen partial pressure in the sintering atmosphere during the second stage at 1400°C.

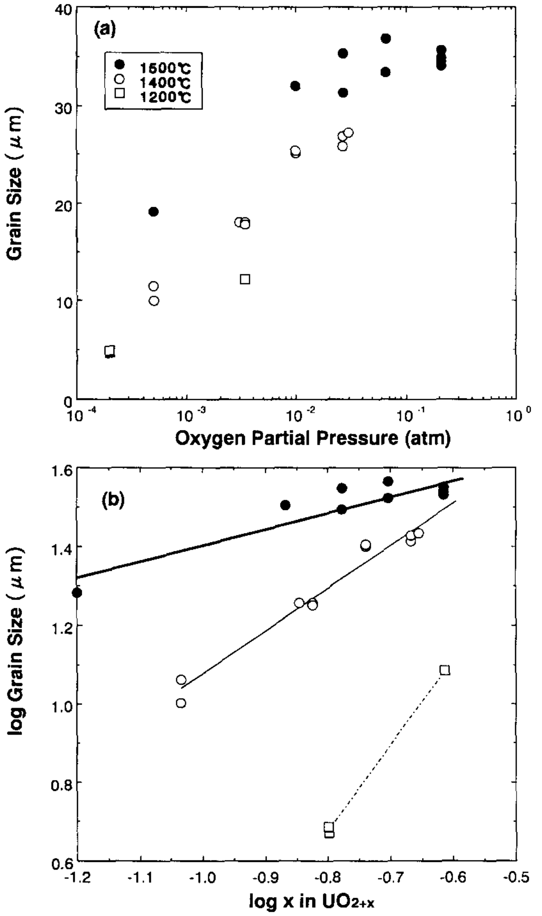

Fig. 4. Grain growth of UO_2 pellets with: (a) oxygen partial pressure; (b) x in UO_{2+x} during the second stage when sintered for 6 h.

1500°C in the 1–6–1 h three-stage process. The grain size increases with increasing the oxygen partial pressure in the second stage. The deviation from stoichiometry x in the UO_{2+x} pellet during sintering, was calculated assuming that the UO_{2+x} was in equilibrium with the oxygen partial pressure of the atmosphere [22]. A sufficient time when elapsed for the equilibration of the UO_{2+x} with the oxygen partial pressure, however, was 1 to 2 h above 1300°C and about 24 h for low oxygen partial pressures below 1200°C [15]. The change of the grain size with x in the UO_{2+x} pellet is shown in Fig. 4(b). The grain size increases with increasing x value in the atmosphere during the second stage. The logarithm of grain size, G (μm), changes linearly with the logarithm of x, i.e., $\log G = A + B \log x$. The values of B are 0.41, 1.1 and 2.2 at 1500, 1400 and 1200°C, respectively, as determined by the method of least squares. The x value dependence of the grain growth decreases with increasing sintering temperature. One of the causes of this effect may be to the difference in the rate of oxidation and densification with temperature. The microstructures of UO_2 pellets sintered by the conventional single-stage process in wet H_2 atmosphere at 1750°C for 5 h and by the present three-stage process in reducing–oxidizing (air)–reducing atmospheres at 1500°C for 1–2–1 h are compared in Fig. 5(a) and (b). The grain size, in the case of sintering in air at 1500°C, is increased by as much as a factor of three compared to that of the normal reference pellet.

Fuhrman et al. [3] used the pellets of air-roasted non-stoichiometric oxide powder (O/U = 2.14 to 2.34) and sintered them in N_2 atmosphere at 1200 and 1300°C using a two-stage process. Their studies demonstrated that a minimum initial O/U ratio of 2.25 to 2.28 was required to attain a pellet density of 95% TD and that the oxide composition was reduced to $UO_{2.20}$ during the N_2 sintering step. Also the addition of a small concentration of H_2 in the N_2 atmosphere promoted the complete reduction of the non-stoichiometric uranium dioxide to the stoichiometric UO_2. Peehs et al. [5] showed that the oxidizing sintering process, consisting of a two-stage process of heating in CO_2 and subsequent heating in H_2/N_2, allowed the sintering temperature to be lowered from 1750°C to 1100 and 1250°C and the sintering cycle time to be shortened by 50% for the directly compacted pellets of UO_2 powder made by the AUC (ammonium uranyl carbonate) conversion process. This means the possibility of direct pressing

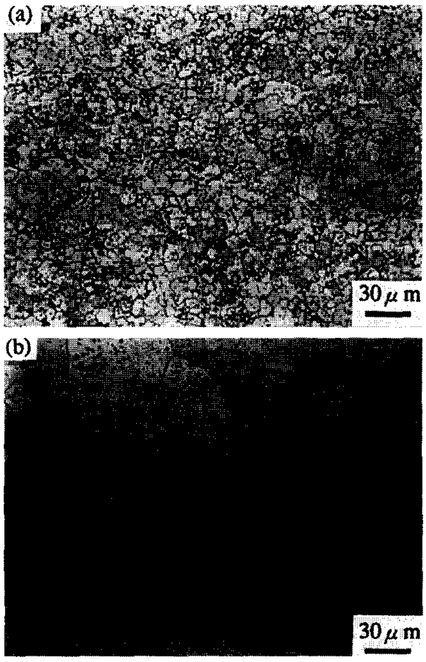

Fig. 5. Microstructure of UO_2 pellets sintered: (a) by the single-stage process in an atmosphere of wet H_2 with dew points between 5 and 10°C for 5 h at 1750°C; (b) by the three-stage process with reducing–oxidizing (air)–reducing atmospheres for 1–2–1 h at 1500°C ($H_2/N_2 = 1/2$ reducing atmosphere).

without the addition of any binder or lubricant and direct sintering without dewaxing step. Assmann et al. [4,6] showed that the considerable grain growth could be achieved by using controlled path sintering which was based on the control of the U–O phases. This was done by controlling the initial O/U ratio of the UO_{2+x} powder (by the addition of U_3O_8) and by controlling the path in the U–O phase diagram taken during sintering in CO_2. They explained that in this oxidizing sintering the grain growth in U_4O_{9-y} phase occurred much faster than in UO_{2+x} for the bimodal grain structure. On the other hand, Song and co-workers [9,10] reported that the duplex grain structure (the bimodal gain structure), consisting of coarse and irregular grains and fine and regular grains, was developed when the powder compacts made by the AUC process, were sintered at 1300°C for 0.1 h in CO_2 atmosphere and then cooled in H_2 atmosphere. A uniform grain structure, however, was developed when H_2–CO_2 atmosphere conditions were used in which the H_2 gas was flowed up to 800°C during the heating-up and then the CO_2 gas was used during the subsequent sintering process followed by cooling in H_2 gas. They discussed the mechanism of the development of the duplex grain structure. This structure was not caused by the difference of the uranium diffusivity in U_4O_{9-y} and UO_{2+x} [4,6], but mainly due to the inhomogeneity of the powder compacts. The coarse grains were assumed to develop around the undeformed particles, while the fine grains form around the particles which were deformed when the powder was compacted with a die-wall lubricant. The uniform grain structure, produced under the H_2–CO_2 atmosphere conditions, was developed as a result of fine cracking in the powder compacts during reduction in H_2 atmosphere, so that the large aggregates formed around the undeformed particles were broken into many small aggregates [9]. As the sintering time was increased from 0.1 to 40 h, the initial duplex grain structure changed into the uniform structure. They thought that this change was caused by continued grain growth in the clusters of fine and regular grains, and the simultaneous transition from coarse irregular grains into regular ones due to the local migrations of the grain boundaries, which were driven by the varying curvatures along a boundary [10]. Han et al. [8] indicated that the grain size monotonically increased with x in UO_{2+x} for the x values between 0.005 and 0.01 when sintered in the controlled CO_2/CO mixtures for 0.5 to 10 h at low temperatures of 1050°C and 1200°C using the powders made from AUC and ADU, respectively. On the other hand, Chevrel et al. [7] showed that the grain growth stopped after a certain sintering time in excess of 15 h during the sintering of UO_{2+x} in CO_2 at 1100°C and the grain size did not exceed 10 μm in the pellets of the UO_2 powder prepared by a dry process. They explained that the addition of U_3O_8 to adjust the initial O/U ratio (2.08 to 2.22), established a fine network of pores increasing the influence of the surface phenomena.

The duplex grain structure and the critical grain size (about 10 μm) mentioned above, are not observed in the large grain pellets produced by the three-stage sintering process described in this study using the powders made from ADU without the addition of U_3O_8 (Fig. 5(b)). The present three-stage process is different from the earlier process reported by Song et al. [9]. The temperature of the earlier process in which the reducing atmosphere was changed to the oxidizing one, was the reducing temperature of 800°C, whereas that of the present process was the sintering temperature between 1200 and 1500°C. Also the oxidizing atmosphere of the earlier process was CO_2 gas, whereas that of the present process was the controlled oxygen atmosphere in which the oxygen partial pressure was higher than that of CO_2 gas. The oxygen partial pressure can be high by increasing the temperature at which the reducing atmosphere is changed to the oxidizing one. The present process was carried out in the reducing–oxidizing–reducing atmospheres. In the first reducing atmosphere, the O/U ratio is reduced to 2.00 at about 800°C during the heating-up. Therefore, the sinterability is independent of the initial O/U ratio. The temperature was held constant for 1 h and then the atmosphere was changed from the reducing atmosphere to the oxidizing atmosphere in which the oxygen partial pressure was controlled. In the oxidizing atmosphere, the O/U ratio increases by absorbing oxygen from the gas phase. The oxygen partial pressure in this atmosphere is the maximum corresponding to the equilibrium value at the boundary between the single-phase region UO_{2+x} and the two-phase region UO_{2+x} + U_3O_{8-z} at the sintering temperature (Fig. 2).

The defect structure of UO_{2+x} has been proposed [24–28]. Park and Olander [24] have proposed that the oxygen interstitial, the Willis defect [25] and the hole (U^{5+}) are only the significant defects and that the Willis defects become dominant in the region of $x > 0.004$ of UO_{2+x} at 1500°C. This defect structure assumed the anion Frenkel pair (i.e., oxygen interstitial and vacant oxygen lattice site). Unless cation diffusion was of interest, the cation Frenkel defect and Schottky defect could be neglected since their formation energies were much higher than that of the anion Frenkel pair. On the other hand, Matzke [26–28] has proposed that the dominant defect in UO_{2+x} are oxygen interstitials and uranium vacancies. This defect structure assumed the oxygen and cation Frenkel defects and Schottky defect and these equilibria were maintained. He has predicted that the concentrations of oxygen interstitials and uranium vacancies increase with x and x^2 and these of oxygen vacancies and uranium interstitials decreases with x^{-1} and x^{-2}, respectively. The uranium atoms diffuse much more slowly than oxygen in the fluorite-type oxides [28]. Breitung [29] summarized that the oxygen self-diffusion coefficients in UO_{2+x} increased with x, and this difference diminished with increasing temperature. Murch [30] evaluated that a statistically significant maximum of oxygen self-diffusion coefficients occurred at about $x = 0.10$ at 800°C. The grain size, however, monotonically increases with increasing x above 0.1 (Fig. 4(b)). On the other hand, Matzke [27,28] proposed that the uranium self-diffusion coefficients increased approximately with x^2. The x value dependence of the uranium self-diffusion coefficients is stronger than that of the oxygen self-diffusion coefficients. The uranium diffusion in UO_{2+x} usually is rate-determining for the final stage sintering and grain growth [27,28]. The defect structure of UO_{2+x} existing during sintering is not clearly identified. In the present study, however, the observed sintering behaviour supports the defect structure assumed by Matzke [27,28]. If the equilibrium is maintained between the UO_{2+x} and the oxygen partial pressure and if the excess oxygen ions enter the lattice interstitially and both Frenkel and Schottky defects are present simultaneously, the oxygen interstitials decrease the concentration of oxygen vacancies, thereby increasing the concentration of uranium vacancies through Schottky equilibrium. An increase of the number of uranium vacancies increases its diffusion coefficient. The enhancement of the densification and grain growth of UO_{2+x} sintered at low temperatures is due to higher uranium diffusion coefficient which increases with increasing oxygen partial pressure and therefore the x value. After the sintering process during this second stage, the atmosphere was changed again to the reducing one. By heating in the third atmosphere, the O/U ratio of the sintered pellets is reduced to 2.000 during the soaking period of 1 h and cooling-down. This reduction step can be performed also at low temperatures because of the high oxygen chemical diffusion coefficients which are less dependent on x [28].

3.3. Thermal dimensional stability

Fig. 6 shows the change of UO_2 pellet density during thermal resintering. Thermal resintering tests on normal grain UO_2 pellets made by the two-stage and the three-stage sintering processes in this study, were carried out in wet H_2 atmosphere at 1700°C for 64 h. The two-stage process consisted of sintering in CO_2–H_2 atmospheres for 2–1 h and the three-stage process consisted of sintering in H_2–CO_2–H_2 atmospheres for 1–4–1 h at 1400°C. The density change of the pellets produced by the three-stage process is on the whole similar to the moderate densification change which was observed in the standard pellets sintered in H_2 atmosphere at 1750°C for 3 h [31] as shown in Fig. 6. The pellet produced by the two-stage process, however, swelled to a large extent. The porosity of this pellet was measured before and after the resintering. It was shown that the open porosity increased from 0.4 to 1.2 vol% and that the closed porosity increased from 6.0 to 10.0 vol%. Also, the pore of increased size developed in the resintering could be observed by ceramography. This thermal swelling seems to occur due to the increase in the closed porosity.

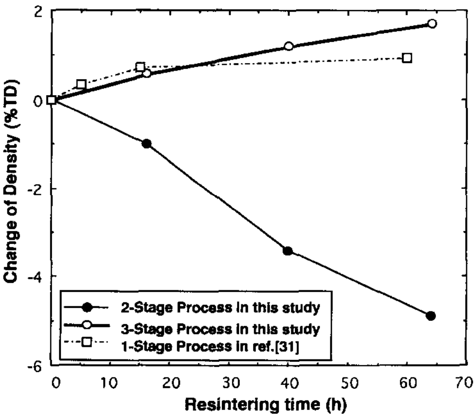

Fig. 6. Change of density of UO_2 pellets with time during resintering at 1700°C in wet H_2.

Kamath et al. [32] indicated that the MOX pellets produced by a single-stage sintering process at 1200°C in CO_2 atmosphere, had a tendency to swell rather than densify during the resintering tests at 1700°C for 24 h. Zinc behenate (0.5 to 1 wt%) was used as a lubricant in order to have the intended O/M ratio in the single-stage sintering. On the other hand, Peehs et al. [5] indicated that the resintering characteristics of the UO_2 pellets produced by the two-stage process of sintering in CO_2–H_2 atmospheres at low temperatures, were the same as those of the H_2 sintered pellet. In this case, however, the pellets were directly pelletized without adding any lubricant.

The temperature at which the densification starts is lower in CO_2 than in H_2 for the same heating-up conditions. If the release of some gases (e.g., CO or CO_2) produced by decomposition of the lubricant, zinc stearate, $Zn(C_{18}H_{35}O_2)_2$, is retarded during heating-up in CO_2 atmosphere, such gases will be trapped in the closed pores in the two-stage sintering process. The H_2 and O_2 gases can escape from the closed pores by dissolution or diffusion. In contrast, the gases such as CO and CO_2 do not normally escape from the closed pores because of lower solubility [14]. One reason of this dimensional increase during the resintering may be the plastic deformation of UO_2 matrix by the gas pressure in the closed pores. If the fission gas bubble size increases with increasing pressure of the trapped Xe and Kr and the residual gases (CO or CO_2) in the closed pores, it is possible that this thermal swelling will have an adverse effect on irradiation-induced fission gas swelling.

4. Conclusions

The three-stage sintering process developed in this study, was confirmed to be a potential sintering method for large grain UO_2 pellets. From the sinterability and the other characteristics of the pellets fabricated by this process, the following conclusions were obtained.

(1) The three-stage sintering process was carried out in reducing–oxidizing–reducing atmospheres at low temperatures between 1200 and 1500°C. Since the pellets are reduced during the heating-up of the first reducing process, the sinterability is independent of the initial O/U ratio. After the sintering temperature was reached, the atmosphere was changed from reducing to oxidizing one where the oxygen partial pressure was controlled to the maximum corresponding to the boundary between the single-phase region UO_{2+x} and the two-phase region UO_{2+x}–U_3O_{8-z}. The densification and grain growth of UO_{2+x} are enhanced by increasing the oxygen partial pressure. The O/U ratio of the sintered pellets was 2.000 ± 0.005 after the subsequent reduction in H_2/N_2 $(=1/2)$ mixture for 1 h followed by cooling-down.

(2) The grain size of the UO_2 pellets sintered in reducing–oxidizing (air)–reducing atmospheres for 1–2–1 h at 1500°C was by a factor of three larger than that of the reference pellets sintered in wet H_2 for 5 h at 1750°C (8 μm).

(3) The dimensional changes during resintering at 1700°C of the UO_2 pellet sintered in H_2–CO_2–H_2 atmospheres of the three-stage process at 1400°C showed a moderate densification, whereas a large swelling occurred in the pellets sintered in CO_2–H_2 of the two-stage process.

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